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Thermal studies of gel-grown cadmium tartrate crystals

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Abstract : Cadmium tartrate crystals were grown by the gel method. The effect of optically sensitive tartaric acid, *i.e.* dextro tartaric acid and levo tartaric acid, was studied. The crystals were having dendritic type morphology. The thermal study was carried out by employing thermogravimetry. The kinetic and thermodynamic parameters were calculated from the thermogram for the dehydration process using Coats and Redfern and Horowitz and Metzger relations.

Keywords : Cadmium tartrate, kinetic parameters, thermodynamic parameters, thermogravimetry.

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Various properties of cadmium tartrate compounds have been investigated by several workers, for example, the thermal properties [1], the phosphorescent properties [2], the stability [3], the electro chromatographic investigations [4] and the synergist properties of Cd^{++} ions for antioxidant action with tartaric acid in cosmetic products [5]. The effect of optically sensitive tartaric acids, *i.e.* dextro tartaric acid and levo tartaric acid, was reported for copper tartrate crystals [6] and zinc tartrate crystals [7]. In the present investigation, dendritic crystals of cadmium tartrate were grown by the gel technique using different optically sensitive tartaric acids, *i.e.* dextro tartaric acid and levo tartaric acid. The effects of optically sensitive tartaric acids on thermal decomposition as well as kinetic and thermodynamic parameters were studied.

The crystallization apparatus employed were glass test tubes of 25 mm diameter and 140 mm in length. The AR grade chemicals were used to grow the crystals. Sodium metasilicate solution was acidified either with dextro tartaric acid or levo tartaric acid in the respective cases. The specific gravity and pH of the mixtures were varied between 1.02 to 1.06 and 4.0 to 5.0, respectively. The appropriate mixtures were transferred into different test tubes for setting the gel. After setting the gel, a supernatant solution of 1M $CdSO_4$ was gently poured without disturbing the gel surfaces. The nucleation was observed within 24 hours. The best quality dendritic type crystals were grown for 4.5 pH and 1.06 specific gravity, which are observed in Figure 1. The crystals were semi-transparent and yellow in color, but they lost their color within two months time and became colorless transparent. On the other hand, for 4.5 pH and 1.02 specific gravity, thin whiskers type bunch of crystals originating from the same location were observed, which are shown in Figure 2.

The following reaction is expected to occur during the process :

$$CdSO_4.nH_2O+H_2C_4H_4O_6 \rightarrow CdC_4H_4O_6.mH_2O+ H_2SO_4+ (n\text{-}m)\ H_2O,$$

where $n \geq m$.

The thermogravimetric analysis (TGA) was carried out, from room temperature to 800 °C at heating rate of 15 °C/min in atmosphere of air by using NETZSCH Geratebau GmbH thermal analyzer.

The thermal studies of copper tartrate crystals [6], zinc tartrate crystals [7], calcium tartrate single crystals [8], neodymium tartrate crystals [9] and iron tartrate spherulitic

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crystals [10] have been reported. Andreev and Vesnovskii [11] studied the thermal decomposition of cadmium tartrate. The thermogravimetric analysis and DTA were employed by Vaclav and Ederova [1] to study the thermal behaviour of tartrates of divalent metals including Cu, Zn and Cd.

Figures 3 and 4 indicate the thermograms of cadmium dextro tartrate and cadmium levo tartrate crystals,

Figure 1. Dendritic type crystals grown for 4.5 pH and 1.06 specific gravity.

Figure 2. Thin whiskers type bunch of crystals are originating from the same location in gel for 4.5 pH and 1.02 specific gravity.

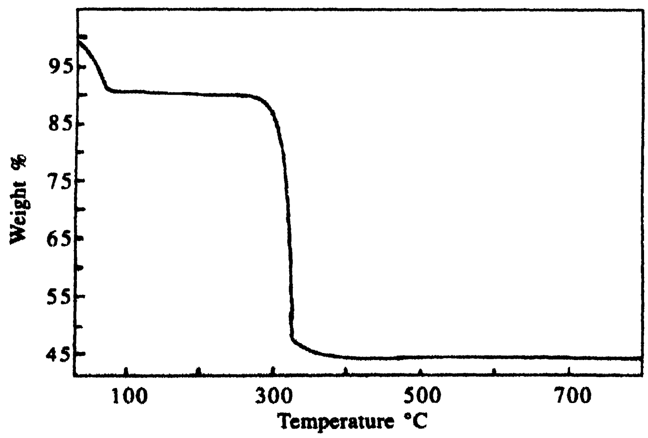

Figure 3. The thermogram of cadmium dextro tartrate crystals.

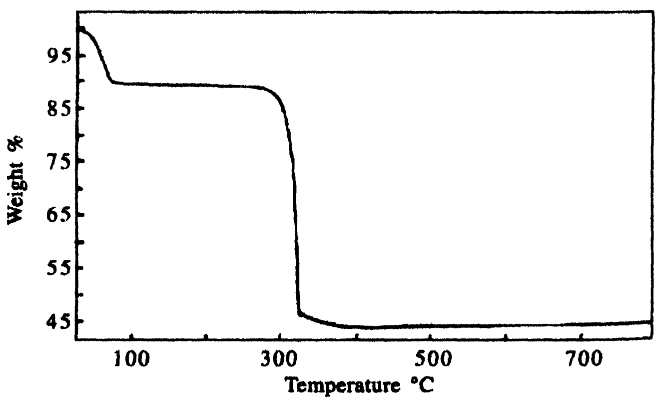

Figure 4. The thermogram of cadmium levo tartrate crystals.

respectively. One can see from Figure 3 that the dehydration process starts right from room temperature and at 80°C temperature the sample becomes anhydrous, further it decomposes sharply into CdO + ½O at 320°C and finally, it turns into CdO at 450°C by losing ½O. The similar behaviour was observed for cadmium levo tartrate crystals, which can be seen from Figure 4. The thermal behaviour of cadmium dextro tartrate and cadmium levo tartrate crystals are summarized in Table 1 by comparing theoretical weight percentage and observed weight percentage at different stages. It was found that both crystals were having 1.5 H_2O molecules attached with them.

Table 1. The decomposition process of cadmium tartrate crystals and TGA results.

Sample	Temperature in °C	Decomposition of crystals	Theoretical weight in %	Observed weight in %
Cadmium	Room			
dextro	temp.	$CdC_4H_4O_6.1.5\ H_2O$	100	100
tartrate	80	$CdC_4H_4O_6$	90.61	91
crystal	320	Cd O + ½ O	47.46	50
	450	CdO	44.68	45
Cadmium	Room			
levo	temp.	$CdC_4H_4O_6.1.5\ H_2O$	100	100
tartrate	80	$CdC_4H_4O_6$	90.61	89.5
crystal	320	CdO + ½ O	47.46	46
	375	CdO	44.68	44.50

Kinetic and thermodynamic parameters can be evaluated from thermogram. Dehydration kinetics of lithium sulphate monohydrate single crystals have been recently reported by Modestov *et al* [12]. Moreover, Slovak [13] tried to determine the kinetic parameters by direct nonlinear regression from the TG curves. In the present investigation, two different equations, namely, the Coats-Redfern relation [14] and Horowitz-Metzger relation [15], were used to evaluate the kinetic parameters from the thermograms of Figurs 3 and 4.

The Coats and Redfern relation [15] is as follows;

$$\log_{10}\{1-(1-\alpha)^{1-n}/T^2(1-n)\} = \{\log_{10}(AR/aE)(1-2RT/E)\}-\{E/2.3RT\}, \quad (1)$$

where E is the activation energy, A is the frequency factor, α is the fraction of decomposed material at time t, n is the order of reaction, and T is the absolute temperature.

Horowitz and Metzger relation [15] is of the following type :

$$\log_{10}[1-(c)^{1-n}/1-n] = E\theta/2.303\,RT_s^2 \quad (2)$$

where $\theta = T-T_s$ and T_s is chosen from the curve of decomposed fraction *versus* time at the maximum value of slope.

These equations were applied to the first stage of the decomposition, *i.e.* dehydration of crystals. The detailed analysis is discussed by Joseph and Joshi [16]. Figures 5 and 6 are the plots of Coats-Redfern relation for cadmium

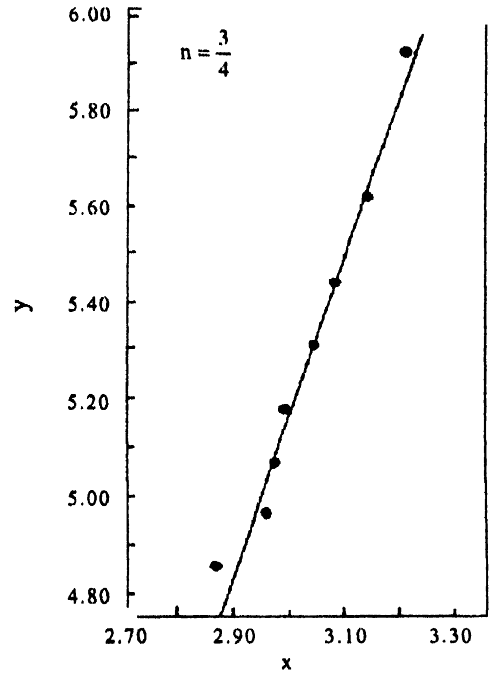

Figure 5. The plot of Coats-Redfern relation of cadmium dextro tartrate crystals.

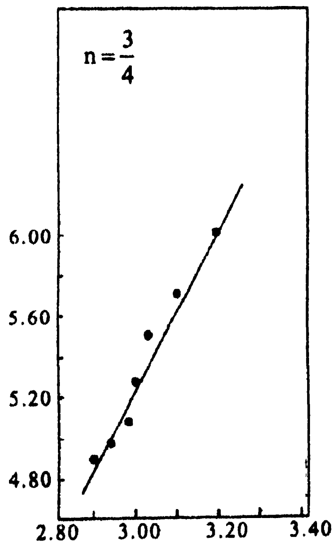

Figure 6. The plot of Coats-Redfern relation of cadmium levo tartrate crystals.

dextro tartrate and cadmium levo tartrate crystals, respectively. The values of order of reaction, activation energy and frequency factor were calculated. Using the values of frequency factor, the values of entropy and other thermodynamic parameters were estimated. The thermodynamic parameters such as the standard entropy ($\Delta^{\#}S^{0}$), the standard enthalpy ($\Delta^{\#}H^{0}$), the standard Gibbs free energy ($\Delta^{\#}G^{0}$), the standard change in internal energy ($\Delta^{\#}U^{0}$) were calculated by applying the well known formulae, as described in details by Vaishnav *et al* [17], Laidler [18], Gokeen and Reddy [19]. Figures 7 and 8 show the plots for Horowitz and Metzger relation, for both cadmium dextro tartrate and cadmium levo tartrate crystals, respectively. The values of kinetic parameters were obtained from these plots. The values of different kinetic and thermodynamic parameters are listed in Tables 2 and 3. It can be noticed from Table 2 that the order of reaction is ¾ which remains the same for both types of crystals as well as the relations. On the other hand, the values of activation energy are higher in cadmium levo tartrate crystals than cadmium dextro tartrate crystals. This difference is assumed to be due to different types of optically sensitive tartaric acids used in the growth of crystals, which may be due to different symmetry environments provided by optically sensitive tartaric acids to make bonds with metallic ion in respective crystals. This result agrees with earlier results of copper dextro tartrate and copper levo tartrate crystals [6].

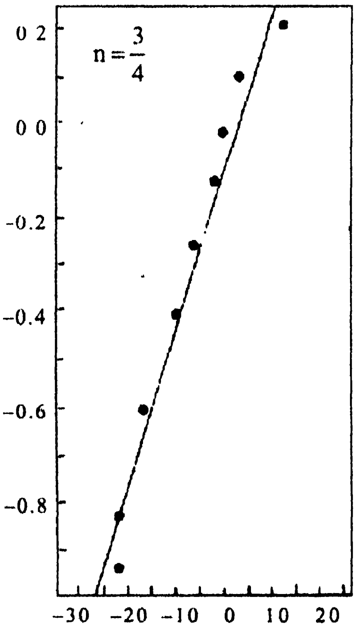

Figure 7. The plot of Horowitz-Metzger relation of cadmium dextro tartrate crystals.

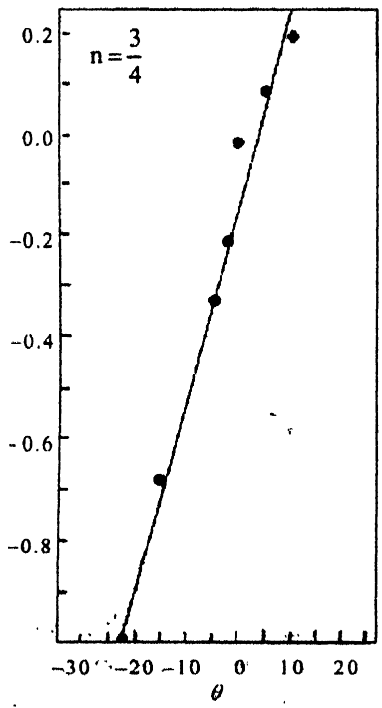

Figure 8. The plot of Horowitz-Metzger relation of cadmium levo tartrate crystals.

Table 2. The values of order of reaction and activation energy for different samples.

Samples	Relations	Order of reaction (n)	Activation energy kJ mol^{-1}
Cadmium dextro tartrate crystal	Coats-Redfern	3/4	63.82
	Horowitz-Metzger	3/4	70.91
Cadmium levo tartrate crystal	Coats-Redfern	3/4	74.34
	Horowitz-Metzger	3/4	80.15

Table 3. Thermodynamic parameters.

Cadmium dextro tartrate crystals	(1) Entropy ($\Delta^{\#}S^{0}$) = 139.27 JK^{-1} mol^{-1}
	(2) Enthalpy ($\Delta^{\#}H^{0}$) = 58.25 kJ mol^{-1}
	(3) Gibbs free energy ($\Delta^{\#}G^{0}$) = 11.60 kJ mol^{-1}
	(4) Standard change in internal energy ($\Delta^{\#}U^{0}$) = 61 04 kJ mol^{-1}
Cadmium levo tartrate crystals	(1) Entropy ($\Delta^{\#}S^{0}$) = 171 80 JK^{-1} mol^{-1}
	(2) Enthalpy ($\Delta^{\#}H^{0}$) = 68.78 kJ mol^{-1}
	(3) Gibbs free energy ($\Delta^{\#}G^{0}$) = 11.21 kJ mol^{-1}
	(4) Standard change in internal energy ($\Delta^{\#}U^{0}$) = 71.55 kJ mol^{-1}

The difference in the values of activation energy for Coats and Redfern as well as Horowitz and Metzger relations are due to different mathematical models used in these equations. These two equations, however, incorporate the Arrhenius law in the analysis, but subsequent mathematical treatments and assumptions are different which, ultimately, yields two different equations. This has been discussed by Dabhi and Joshi [7] earlier.

In conclusion, cadmium dextro tartrate and cadmium levo tartrate crystals are thermally unstable and decompose ultimately into CdO upon heating. The values of kinetic and thermodynamic parameters of dehydration are higher for cadmium levo tartrate than cadmium dextro tartrate crystals. However, the values of standard Gibbs free energy are nearly the same for cadmium levo tartrate and cadmium dextro tartrate crystals. This difference in the values of kinetic and thermodynamic parameters may be due to different optically sensitive dextro tartrate and levo tartrate radicals bonding with cadmium ion in different symmetry environments. This agrees with to the earlier results, of copper dextro and copper levo tartrate crystals.

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